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The Oxidation State of Ni in the Nickel Oxide Electrode and Related Nickel Oxide  
Compounds: II. Geometric Evidence

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## The oxidation state of Ni in the nickel oxide electrode and related nickel oxide compounds: II. Geometric evidence

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The electronic structures of the nickel oxide electrode (NOE),  $\text{NiO}_x(\text{OH})_{2-x}$  for  $x=0-1.6$  and the related nickel oxide materials including the  $\text{NiO} - \text{LiNiO}_2 - \text{NiO}_2$  series and the " $\text{Ni}^{4+}$ " compounds,  $\text{KNiO}_2(\text{IO}_4)$  and  $\text{BaNiO}_3$ , have been investigated utilizing geometric data such as the Ni-OH and Ni-O bond lengths published in the literature. The electronic structures deduced from these bond lengths agree with those found using spectroscopic data, which were presented in the preceding paper. In addition, the observed shortening of the Ni-O bond length in the  $\text{NiO} - \text{LiNiO}_2 - \text{NiO}_2$  series is shown to arise from covalent shortening. The implications of this newly proposed electronic structures are as follows: (i) the charging reaction for the NOE can be viewed as  $\text{OH}^- (\text{Ni}^{2+}) \rightarrow \text{O}^- (\text{Ni}^{2+}) + \text{H}^+ + \text{e}^-$ , where  $(\text{Ni}^{2+})$  reminds us that the  $\text{OH}^-$  and  $\text{O}^-$  anions are attached to the  $\text{Ni}^{2+}$  ion, which remain unchanged; (ii) the electron conduction in the charged NOE is in the oxygen layer; and (iii) the coloration of the NOE upon charging is due to the  $3d (\text{Ni}^{2+}) \rightarrow 2p (\text{O}^-)$ , metal-to-oxygen, charge transfer in the charged NOE.

## I. INTRODUCTION

In the preceding paper [referred here as paper I], we have analyzed the Ni 2p XPS (x-ray photoemission spectroscopy) and the Ni K-edge XAS (x-ray absorption spectroscopy) data for the nickel oxide electrode (NOE) and related nickel oxide compounds and found that these data consistently favor the more covalent electronic structure over the conventional ionic electronic structure for these materials, suggesting that oxidation of the  $\text{Ni}^{2+}$  ion is harder than oxidation of the  $\text{O}^{2-}$  anion in the NOE and related compounds. In this paper, we shall analyze the geometric data, namely the variations in the Ni-OH and Ni-O bond lengths.

The systems studied and notations used are the same as those in the paper I. Briefly, the systems analyzed are (a) the NOE materials,  $\text{NiO}_x(\text{OH})_{2-x}$  for  $x=0-1.6$ ; (b) the  $\text{NiO} - \text{LiNiO}_2 - \text{NiO}_2$  series; and (c) the " $\text{Ni}^{4+}$ " compounds,  $\text{KNiO}_2(\text{IO}_4)$  and  $\text{BaNiO}_3$ . A common property of all of these compounds is that the Ni atom is coordinated octahedrally by oxygen atoms. All of the compounds, except the " $\text{Ni}^{4+}$ " compounds, are known to have a layered structure [1-3]. Here, OS.Ni will be used for oxidation state of Ni and IOS.Ni for the ionic OS.Ni, which is defined as the mean OS.Ni obtained assuming the normal oxidation states of  $\text{Li}^+$ ,  $\text{K}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{O}^{2-}$ ,  $\text{OH}^-$ , and  $\text{IO}_4^-$ . This IOS.Ni is uniquely determined when composition of the compound is given. Therefore most of the figures in this paper and paper I are plotted as a function of this IOS.Ni.

At the end of this paper, we will summarize all evidence available including evidence presented in paper I and the others and review their consistency. After establishing the electronic structures for the NOE and the related nickel oxide compounds, we will discuss the implications of the newly proposed electronic structures.

## II. Ni-O AND Ni-OH BOND LENGTHS

In this paper, the Ni-O distances of the Ni-OH and Ni-O bonds shall be referred to as the Ni-OH and Ni-O bond lengths respectively. The Ni-O distances in the NOE [i.e.,  $\text{NiO}_x(\text{OH})_{2-x}$ ] means the Ni-OH and Ni-O bond lengths in the NOE and the mean Ni-O distance for the NOE means the averaged Ni-O distance of the Ni-OH and Ni-O bond lengths in the NOE. Thus, the term "the Ni-O distance" in this paper has a restricted meaning.

Figure 1 plots the Ni-OH (open circle) and Ni-O (closed circle) bond lengths as a function of the IOS.Ni for the nickel oxide electrode materials,  $\text{NiO}_x(\text{OH})_{2-x}$  [ $\alpha$ -,  $\beta$ - $\text{Ni}(\text{OH})_2$  ( $x=0$ ),  $\beta$ - $\text{NiO}(\text{OH})$  ( $x=1$ ), and  $\gamma$ -" $\text{NiOOH}$ " ( $x=1.5$ )], along with the Ni-O bond lengths for the IOS.Ni $\equiv$ 4 compounds [i.e.,  $\text{Li}_{0.06}\text{NiO}_2$ ,  $\text{KNiO}_2(\text{IO}_4)$ , and  $\text{BaNiO}_3$ ]. The Ni-O distances for the NOE materials are obtained by averaging the recent results reported by O'Grady [4] and Mansour [5], which agree with each other to within 0.01 Å. Those for  $\text{Li}_{0.06}\text{NiO}_2$  [3],  $\text{KNiO}_2(\text{IO}_4)$  [5], and  $\text{BaNiO}_3$  [6] are obtained from the cited references. Needless to say,  $\beta$ - $\text{NiO}(\text{OH})$  and  $\gamma$ -" $\text{NiOOH}$ " have both Ni-OH and Ni-O bonds, whereas the  $\text{Ni}(\text{OH})_2$  and the IOS.Ni $\equiv$ 4 compounds have only one kind of bond, Ni-OH or Ni-O bonds respectively. Figure 1 shows that the Ni-OH bond lengths of  $\beta$ - $\text{NiO}(\text{OH})$  and  $\gamma$ -" $\text{NiOOH}$ " are almost equal to those of  $\alpha$ - and  $\beta$ - $\text{Ni}(\text{OH})_2$  and the Ni-O bond lengths of these are close to those of the IOS.Ni $\equiv$ 4 compounds. In short, the Ni-OH and Ni-O bond lengths are almost invariant against the IOS.Ni.

Here we analyze this invariance on alternative premises of OS.Ni=2 or OS.Ni=IOS.Ni. Let us start with the OS.Ni=IOS.Ni premise. This premise for  $\text{NiO}_x(\text{OH})_{2-x}$  suggests the  $\text{Ni}^{\text{IOS.Ni}+}\text{O}^{2-x}(\text{OH})^{-x}$  electronic structure or the  $\text{Ni}^{\text{IOS.Ni}+}\text{OH}^-$  and  $\text{Ni}^{\text{IOS.Ni}+}\text{O}^{2-}$  bonds, where IOS.Ni=2+x. Therefore, the electrostatic interaction for these bonds will vary with the IOS.Ni. The  $\text{Ni}^{\text{IOS.Ni}+}\text{OH}^-$  and  $\text{Ni}^{\text{IOS.Ni}+}\text{O}^{2-}$  bond

lengths can be estimated rather accurately using the ionic radii for a six coordinated Ni ion proposed by Shannon [7], i.e.,  $O^{2-}$  (1.26 Å),  $OH^-$  (1.23 Å),  $Ni^{2+}$  (0.83 Å), low-spin  $Ni^{3+}$  (0.70 Å), and low-spin  $Ni^{4+}$  (0.62 Å). The resultant Ni-OH (dashed line) and Ni-O (dotted line) bond lengths are inserted in Fig. 1. Let us now consider the OS.Ni=2 premise. The OS.Ni=2 premise for  $NiO_x(OH)_{2-x}$  suggests the  $Ni^{2+}O_x(OH)^{2-x}$  electronic structure or the  $Ni^{2+}-OH^-$  and  $Ni^{2+}-O^-$  bonds, *independent of x and IOS.Ni (=2+x)*. Consequently, the Ni-OH and Ni-O bond lengths are expected to be invariant against the IOS.Ni. This invariance for the OS.Ni=2 assignment is included in Fig. 1 by solid lines. The experimental results agree with the solid lines (OS.Ni=2) but not with the dashed and dotted lines (OS.Ni=IOS.Ni) and hence strongly favor the OS.Ni=2 assignment for the compounds,  $\beta$ -NiO(OH),  $\gamma$ -"NiOOH",  $Li_{0.06}NiO_2$ ,  $KNiO_2(IO_4)$ , and  $BaNiO_3$ . This assignment is consistent with the OS.Ni=2 conclusion deduced from the XPS and XAS data in the preceding paper.

Figure 2 plots the *mean* Ni-O distance for the compounds given in Fig. 1 as a function of the IOS.Ni. The mean Ni-O distance ( $R_{av}$ ) for  $\beta$ -NiO(OH) and  $\gamma$ -"NiOOH" is calculated as  $R_{av} = (N_1 R_1 + N_2 R_2) / (N_1 + N_2)$ , where the  $R_1$  and  $R_2$  (Ni-O distances of the Ni-OH and Ni-O bonds) and the  $N_1$  and  $N_2$  (coordination numbers of the same) have been previously determined by EXAFS analyses [4, 5]. The resultant mean Ni-O distance decreases almost linearly as the IOS.Ni increases, except for that of  $\gamma$ -"NiOOH". An accurate mean Ni-O distance for  $\gamma$ -"NiOOH" is hard to obtain, because the measurement must be *in situ* and is affected by self-discharging. Moreover, two Ni-O bond distances are involved. The coordination number ( $N_1$  and  $N_2$ ) appear to be more sensitive to these experimental instabilities than the Ni-O distances ( $R_1$  and  $R_2$ ). A relatively large deviation from the linear relation for  $\gamma$ -"NiOOH" is likely due to this experimental difficulty. To remind as of this, we have added an arbitrary error bar for the  $\gamma$ -"NiOOH" datum. Unlike the Ni-O distances (Fig. 1), the linearity of the mean Ni-O distances (solid circles)

presented in Fig. 2 can be accounted for by either the OS.Ni=IOS.Ni or OS.Ni=2 premise, as shown below.

The OS.Ni=IOS.Ni premise for the  $\text{Ni}(\text{OH})_2$  -  $\text{NiO}(\text{OH})$  -  $\text{NiO}_2$  series implies the  $\text{Ni}^{2+}(\text{OH})_2^-$  -  $\text{Ni}^{3+}\text{O}^{2-}(\text{OH})^-$  -  $\text{Ni}^{4+}\text{O}^{2-}_2$  electronic structures. Accordingly, the Ni-OH and Ni-O bond lengths for them can be estimated as a sum of the ionic radii cited above. The resultant mean Ni-O distances gives the dashed lines in Fig. 2. On the other hand, the OS.Ni=2 premise for the  $\text{NiO}_x(\text{OH})_{2-x}$  series implies, as discussed above, two constant Ni-O distances,  $R_{\text{OH}}$  for the Ni-OH bond and  $R_{\text{O}}$  for the Ni-O bond, independent of  $x$ . The mean Ni-O distance for the  $\text{NiO}_x(\text{OH})_{2-x}$  is then given by

$$R_{\text{av}} = [xR_{\text{O}} + (2-x)R_{\text{OH}}]/2 = R_{\text{OH}} - (R_{\text{OH}} - R_{\text{O}})(\text{IOS.Ni} - 2)/2, \quad (1)$$

since  $\text{IOS.Ni}=2+x$ . This equation with the constants  $R_{\text{OH}}$  and  $R_{\text{O}}$  (obtained from Fig. 1) gives the solid line in Fig. 2. Thus, both the solid line (OS.Ni=2) and the dashed line (OS.Ni=IOS.Ni) reproduce nicely the experimental results (solid circles) in Fig. 2. However, as demonstrated above, the OS.Ni=IOS.Ni assignment for  $\text{NiO}_x(\text{OH})_{2-x}$  does not reproduce the experimental results in Fig. 1.

### III. Ni-O BOND LENGTH FOR THE $\text{NiO}$ - $\text{LiNiO}_2$ - $\text{NiO}_2$ SERIES

The  $\text{NiO}$ ,  $\text{LiNiO}_2$ , and the  $\text{IOS.Ni} \approx 4$  compounds [i.e.,  $\text{Li}_{0.06}\text{NiO}_2$ ,  $\text{KNiO}_2(\text{IO}_4)$ , and  $\text{BaNiO}_3$ , which are collectively referred to here as  $\text{NiO}_2$ ] have six equal Ni-O bond lengths. Fig. 3 plots the Ni-O bond length for the  $\text{NiO}$  -  $\text{LiNiO}_2$  -  $\text{NiO}_2$  series as a function of the IOS.Ni, where the data for  $\text{NiO}$  [8] and  $\text{LiNiO}_2$  [3, 9] are obtained from the cited references. The Ni-O bond length for this series again can be accounted for by either the OS.Ni=IOS.Ni or OS.Ni=2 premise, as will be seen at the end of this section.

The OS.Ni=IOS.Ni premise for this series implies the  $\text{Ni}^{2+}\text{O}^{2-}$  -  $\text{Li}^+\text{Ni}^{3+}\text{O}^{2-}_2$  -  $\text{Ni}^{4+}\text{O}^{2-}_2$  electronic structures. Accordingly, the Ni-O bond length for this series can be estimated as a sum of the ionic radii of  $\text{O}^{2-}$  and  $\text{Ni}^{n+}$ , as we have done above. The resultant Ni-O bond lengths (dashed lines) are plotted in Fig. 3. Agreement between experiment and these estimates is excellent, supporting the conventional OS.Ni=IOS.Ni assignments and casting some doubt on the OS.Ni=2 assignments.

On the other hand, the OS.Ni=2 premise for this series implies the  $\text{Ni}^{2+}\text{O}^{2-}$  -  $\text{Li}^+\text{Ni}^{2+}[\text{O}^-\text{O}^{2-}]$  -  $\text{Ni}^{2+}\text{O}^{2-}_2$  electronic structures. The  $\text{Li}^+\text{Ni}^{2+}[\text{O}^-\text{O}^{2-}]$  structure would suggest two Ni-O bond lengths, one for  $\text{Ni}^{2+}-\text{O}^-$  and another for  $\text{Ni}^{2+}-\text{O}^{2-}$ . However, experimental results [9] shows six equal Ni-O bond lengths for  $\text{LiNiO}_2$ , indicating that the  $\text{O}^-(2p^{-1})$  hole is delocalized. Therefore, the  $\text{Li}^+\text{Ni}^{2+}\text{O}^{1.5-}_2$  structure is more realistic than the  $\text{Li}^+\text{Ni}^{2+}[\text{O}^-\text{O}^{2-}]$  structure. We then have the series,  $\text{Ni}^{2+}\text{O}^{2-}$  -  $\text{Li}^+\text{Ni}^{2+}\text{O}^{1.5-}_2$  -  $\text{Ni}^{2+}\text{O}^{2-}_2$ . The observed Ni-O bond length ordering for this series is  $\text{NiO} (2.09\text{\AA}) > \text{LiNiO}_2 (1.97\text{\AA}) > \text{NiO}_2 (1.85\text{\AA})$ , that is,

$$\text{Ni}^{2+}-\text{O}^{2-} > \text{Ni}^{2+}-\text{O}^{1.5-} > \text{Ni}^{2+}-\text{O}^- \quad (2)$$

This ordering is obviously counter-intuitive, since a simple electrostatic argument suggests the reverse. The remainder of this section will be devoted to showing that this counter-intuitive ordering is caused by covalent shortening.

#### A. Ionic contribution

In this subsection, we shall estimate the ionic contributions to the  $\text{Ni}^{2+}-\text{O}^{2-}$  bond in NiO and the  $\text{Ni}^{2+}-\text{O}^-$  bond in  $\text{NiO}_2$ . In both NiO and  $\text{NiO}_2$ , the Ni atoms are coordinated octahedrally by oxygen atoms, but they have the NaCl and  $\text{CdI}_2$  structures, respectively. According to Eq. (13-3) in Pauling's book [10], the Ni-O bond lengths  $R_1$  and  $R_2$  for NiO and  $\text{NiO}_2$  can be approximated by



$$R_1 = (nB_1/A_1Q_1^2)^{1/(n-1)} \text{ and } R_2 = [nB_2/A_2(Q_2/2)^2]^{1/(n-1)}, \quad (3)$$

where the Born exponent  $n$  is around  $n=8$  for the nickel oxides;  $A_1$  ( $=1.74756$ ) and  $A_2$  ( $=4.71$ ) are the Madelung constants for the NaCl and CdI<sub>2</sub> structures;  $B_1$  and  $B_2$ , the repulsive coefficients, should be similar ( $B_1 \approx B_2$ ), since the number of coordinated anions to the Ni ion are the same; and  $Q_1$  and  $Q_2$  are the effective atomic charges on the Ni atoms, which are not necessarily equal to the OS.Ni. It is reasonable to assume  $Q_1=Q_2$ , because we are assuming the same OS.Ni ( $=2$ ) for both NiO and NiO<sub>2</sub>. Using the above relations, we obtain

$$R_2/R_1 = (4A_1/A_2)^{1/(n-1)} = 1.058. \quad (4)$$

Note that the  $R_2/R_1$  ratio is independent of the B and Q coefficients. From the known Ni-O distance for NiO ( $R_1=2.089\text{\AA}$ ) and the above  $R_2/R_1$  ratio (4), we estimate the Ni-O distance for the *layered* NiO<sub>2</sub> ( $R_2=2.210\text{\AA}$ ). In sum, the Ni<sup>2+</sup>-O<sup>-</sup> bond length for NiO<sub>2</sub> is predicted to be longer than the Ni<sup>2+</sup>-O<sup>2-</sup> bond length for NiO by  $0.12\text{\AA}$ .

So far, we have implicitly assumed that the "size" of the O<sup>2-</sup> and O<sup>-</sup> ions are equal to each other by setting the repulsive coefficients equal,  $B_1=B_2$ . Here we estimate the relative sizes of the O<sup>2-</sup> and O<sup>-</sup> ions following Pauling's idea of univalent radii [10], which assumes that the ion size ( $R$ ) is proportional to the mean radius (namely,  $\langle\phi|r|\phi\rangle$ ) of the outermost orbital  $\phi$ , (the  $2p$  orbital for the O<sup>2-</sup> and O<sup>-</sup> ions). Using Slater's atomic wavefunctions and Burn's rules [11] for evaluating the screening constants  $S$  [i.e.,  $S(\text{O}^-)=4.40$ ;  $S(\text{O}^{2-})=4.75$ ], we obtain

$$R(\text{O}^{2-})/R(\text{O}^-) = [Z-S(\text{O}^-)]/[Z-S(\text{O}^{2-})] = 1.108, \quad (5)$$

where  $Z$  ( $=8$ ) is the nuclear charge of the oxygen atom. From the known O<sup>2-</sup> radius  $R(\text{O}^{2-})=1.26\text{\AA}$ , we obtain  $R(\text{O}^-)=1.14\text{\AA}$ , which is shorter than the O<sup>2-</sup> radius by  $0.12\text{\AA}$ . Combining this and the result in the previous paragraph, we conclude that the Ni<sup>2+</sup>-O<sup>2-</sup>

bond length for NiO should be equal to the  $\text{Ni}^{2+}\text{-O}^-$  bond length for the *layered*  $\text{NiO}_2$  since the two effects, electrostatic and ion-size effects, are almost exactly canceled out by each other. To sum up, there is no ionic contribution to the Ni-O bond-length difference between the  $\text{Ni}^{2+}\text{-O}^{2-}$  bond in NiO and the  $\text{Ni}^{2+}\text{-O}^-$  bond in  $\text{NiO}_2$ .

### B. Covalent contribution

There is another mechanism that can alter the Ni-O bond length, i.e., covalent shortening. Since the  $\text{O}^-$  ion, unlike the  $\text{O}^{2-}$  ion, has an open-shell electronic structure, the  $\text{Ni}^{2+}\text{-O}^-$  bond length in  $\text{Ni}^{2+}\text{O}_2^-$  can be shorter than the  $\text{Ni}^{2+}\text{-O}^{2-}$  bond length in  $\text{Ni}^{2+}\text{O}^{2-}$ , due to a covalent shortening. Below we estimate the magnitude of this covalent shortening.

In terms of the  $\text{NiO}_6$  cluster approximation,  $\text{Ni}^{2+}\text{O}_2^-$  and  $\text{Ni}^{2+}\text{O}^{2-}$  corresponds to  $\text{Ni}^{2+}\text{O}_6^-$  and  $\text{Ni}^{2+}\text{O}_6^{2-}$ , respectively. The electronic state,  $\text{Ni}^{2+}\text{O}_6^-$ , can be reached from the  $\text{Ni}^{2+}\text{O}_6^{2-}$  by removing one electron from each oxygen atom, 6 electrons altogether. We therefore refer  $\text{Ni}^{2+}\text{O}_6^{2-}$  and  $\text{Ni}^{2+}\text{O}_6^-$  as the ground and ionized state, respectively. Figure 4 depicts the symmetric Ni-O stretching potential curves,  $V^{(G)}(R)$  and  $V^{(I)}(R)$ , for the ground and ionized state, where  $R$  is the Ni-O distance, and  $R_e^{(G)}$  and  $R_e^{(I)}$  are the equilibrium Ni-O distances of the ground state and ionized state. The potential energy difference,  $V^{(I)}(R) - V^{(G)}(R)$ , is nothing but the ionization energy,  $\text{IE}(R)$  [ $\equiv V^{(I)}(R) - V^{(G)}(R)$ ]. As indicated in Fig. 4, the  $\text{IE}(R)$  function varies slowly with  $R$  in comparison with the  $V(R)$  functions. For a small variation of  $R$ , such as  $R_e^{(G)} - R_e^{(I)} \approx 0.2 \text{ \AA}$ , the derivative  $d\text{IE}(R)/dR$ , is almost invariant, whereas the  $dV(R)/dR$  is almost a linear function of  $R$ . In the harmonic approximation,  $V^{(G)}(R)$  is given by  $k(R - R_e^{(G)})^2/2$ , where  $k$  is a symmetric force constant.

The  $R_e^{(I)}$  can be obtained from the following equations,

$$dV^{(1)}(R)/dR = dIE(R)/dR + dV^{(G)}(R)/dR = 0 \quad (6)$$

$$dV^{(G)}(R)/dR = k(R - R_e^{(G)}) \quad (7)$$

$$dIE(R)/dR = -6 d\epsilon_{t_{1u}}(R)/dR \quad (8)$$

where  $\epsilon_{t_{1u}}$  is the orbital energy of the highest orbital arising from the ligand oxygen 2p orbitals, which has the  $t_{1u}$  symmetry of the octahedral  $NiO_6$  system. This  $t_{1u}$  orbital is fully occupied in the ground state containing 6 electrons, but is emptied in the ionized state. Note that the  $IE(R)$  is approximated by  $-6\epsilon_{t_{1u}}(R)$ , as usual. Equations (6)-(8) give

$$R_e^{(1)} - R_e^{(G)} = (6/k) d\epsilon_{t_{1u}}(R)/dR, \quad (9)$$

where  $d\epsilon_{t_{1u}}(R)/dR$  is almost invariant and hence will be evaluated at  $R=R_e^{(G)}$ . Since the  $t_{1u}$  orbital is antibonding with respect to the Ni-O bond, the derivative  $d\epsilon_{t_{1u}}/dR$  will be negative and thereby Eq. (8) will predict  $R_e^{(1)} < R_e^{(G)}$  or  $Ni^{2+}-O^- < Ni^{2+}-O^{2-}$  bond-length ordering, i.e., a covalent shortening.

We now estimate  $k$  and  $d\epsilon_{t_{1u}}(R)/dR$  and evaluate  $R_e^{(1)} - R_e^{(G)}$ . The symmetric stretching force constant  $k$  ( $=2.321 \times 10^5$  [dyne/cm]) is estimated from the Ni-O symmetric stretching frequency ( $\omega_e = 560$   $cm^{-1}$ ), which has been observed for the charged NOE [12], using the relation  $k = 5.8883 \times 10^{-2} \mu \omega_e^2$  [dyne/cm], where  $\mu$  is the reduced mass of Ni and O in amu. The  $d\epsilon_{t_{1u}}(R)/dR$  at  $R=R_e^{(G)}$  can be calculated rather accurately by any method which includes the overlap integral between the metal and the ligand oxygen atomic orbitals. We have employed the extended Hückel method with no charge iteration and obtained  $d\epsilon_{t_{1u}}(R)/dR = -0.8401 \times 10^{-4}$  [erg/cm] at the  $R=R_e^{(G)} = 2.09 \text{ \AA}$ . Substituting this  $d\epsilon_{t_{1u}}(R)/dR$  and the  $k$  value into Eq. (4), we have  $R_e^{(1)} - R_e^{(G)} = -0.22 \text{ \AA}$ . This is the covalent contribution to the Ni-O bond length. Since there is no ionic contribution, we predict that the  $Ni^{2+}-O^-$  bond length in  $NiO_2$  is shorter than the  $Ni^{2+}-O^{2-}$  bond length in  $NiO$  by  $0.22 \text{ \AA}$  due to covalent shortening. This prediction is shown in Fig. 3 by the solid line.

Figure 3 shows that both the solid line (i.e., covalent shortening assuming the OS.Ni=2) and the dashed line (i.e., the sum of ionic radii assuming the OS.Ni=IOS.Ni) reproduce excellently the experimental results. However, the OS.Ni=2 assignment is more consistent with the other data. Therefore, we can attribute the decrease of the Ni-O bond length in the NiO-LiNiO<sub>2</sub>-NiO<sub>2</sub> series (Fig. 3) to a covalent shortening.

#### IV. JAHN-TELLER DISTORTION

the absence or presence of a Jahn-Teller distortion (JTD) for the IOS.Ni=3 compounds [i.e., LiNiO<sub>2</sub> and β-NiO(OH)] provides further evidence regarding our question. The ground states of the Ni<sup>2+</sup> and Ni<sup>3+</sup> ions in the NiO<sub>6</sub> octahedron are expected to be Ni<sup>2+</sup>(t<sub>2g</sub><sup>6</sup>e<sub>g</sub><sup>2</sup>)<sup>3</sup>A<sub>2g</sub> and Ni<sup>3+</sup>(t<sub>2g</sub><sup>6</sup>e<sub>g</sub><sup>1</sup>)<sup>2</sup>E<sub>g</sub>. A strong JTD is expected for the degenerate E state of the Ni<sup>3+</sup> ion, but not for the non-degenerate A state of the Ni<sup>2+</sup> ion. For LiNiO<sub>2</sub>, no JTD of the NiO<sub>6</sub> octahedron has been observed [3, 9, 13], suggesting the OS.Ni=2 assignment.

β-NiO(OH) also appears to lack a JTD. The α-AlO(OH) and α-MnO(OH) compounds are known to have a layered structure similar to that of β-NiO(OH) [14]. α-MnO(OH), having high-spin Mn<sup>3+</sup>(t<sub>2</sub><sup>3</sup>e<sup>1</sup>), shows a strong JTD, whereas α-AlO(OH), having a closed-shell ion, Al<sup>3+</sup>, lacks a JTD. As shown in Fig. 5, the Mn-OH and Mn-O bond lengths are clearly split due to the JTD, whereas the Al-OH and Al-O bond lengths are barely split. The M-OH and M-O data for M=Al and Mn are obtained from Wells' book [14]. A splitting of the Ni-OH and Ni-O bond lengths has not been observed for β-NiO(OH) [4]. This absence of a JTD for β-NiO(OH) favors the Ni<sup>2+</sup> assignment over the conventional Ni<sup>3+</sup> assignment.

## V. SUMMARY OF EVIDENCE

Table I summarizes, for each compound, the supporting evidence cited for the OS.Ni=2 vs. OS.Ni=IOS.Ni assignments. This evidence is described with shorthand notations, which are explained in the footnotes of the table. The XPS and XAS evidence are presented in the preceding paper and the geometric evidence is given in this paper. The remainder of the evidence listed in the table, (i.e., "Magnetic moment" and "Oxygen K-edge XAS") can be found in the references given there.

Let us first evaluate the evidence listed for the LiNiO<sub>2</sub> compound. The oxygen K-edge XAS spectrum provides direct evidence for the presence of the O<sup>-</sup> anion [15]. This spectrum and the absence of a Jahn-Teller distortion would be very hard to account for with the Li<sup>+</sup>Ni<sup>3+</sup>O<sup>2-</sup><sub>2</sub> electronic structure, if not impossible. On the other hand, the observed magnetic moment, which might strongly suggest Ni<sup>3+</sup> [13, 16], can be accounted for with a strong antiferromagnetic coupling between the Ni<sup>2+</sup> and O<sup>-</sup> spins [15] based on the OS.Ni=2 assumption. Furthermore, the observed Ni-O bond length, which agrees amazingly well with a sum of the ionic radii of Ni<sup>3+</sup> and O<sup>2-</sup> ions, can also be accounted for by a covalent shortening as demonstrated in this work. In addition, the XPS main-peak energy and satellite energy separation strongly suggest the OS.Ni=2 assignment. For LiNiO<sub>2</sub>, therefore, the evidence for OS.Ni=2 outweighs that for OS.Ni=3.

The LiNiO<sub>2</sub> case shows that the magnetic-moment and Ni-O (ionic radii) evidence does not prove the OS.Ni=NOS.Ni assignment for LiNiO<sub>2</sub>. Therefore, this evidence likely does not prove the OS.Ni=NOS.Ni for the other compounds either. But these are the only two points supporting the OS.Ni=NOS.Ni assignments as seen in the table. On the other hand, there is a preponderance of evidence for the OS.Ni=2 assignment, especially for β-NiO(OH) and γ-"NiOOH". Further, the Ni-O (JTD) evidence for β-NiO(OH) and the XPS (line width) evidence for γ-"NiOOH" would be very hard to account for assuming the

OS.Ni=IOS.Ni premise. More importantly, the OS.Ni=2 assignment can *consistently* account for *all* of the experimental data available. In sum, we propose the OS.Ni=2 assignment for all compounds listed in Table I.

Although we have concluded that the OS.Ni=2 for all the compounds listed in Table I, we certainly do not suggest OS.Ni=2 for every Ni oxide. Our choice of materials is rather restricted, since the Ni site in our materials is octahedrally coordinated by oxygen atoms and all of our materials, except  $\text{KNiO}_2(\text{IO}_4)$  and  $\text{BaNiO}_3$ , have a layered structure. ( $\text{BaNiO}_3$  has a one-dimensional chain structure [6]; the structure of  $\text{KNiO}_2(\text{IO}_4)$  is unknown but likely has a layered structure.) Under these restrictions, we have found that the OS.Ni is 2.

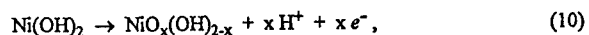
## VI. IMPLICATIONS

Various physical properties, such as the optical, magnetic, and electrical properties, of the nickel oxide electrode (NOE) and related nickel compounds have been discussed on the premise of the OS.Ni=IOS.Ni assignment, which is currently accepted by a majority of workers in the field. To our knowledge, only exception to this is that Sawatzky's group has attempted to account for the magnetic property of Li-substituted NiO [i.e.,  $\text{Li}_y\text{Ni}_{2-y}$  for  $y=0-1$ ] based on the premise of OS.Ni=2 [15]. Now that the OS.Ni=2 assignment is established here, previous explanations based on the OS.Ni=IOS.Ni assignment must be re-examined in light of this new finding. Below we simply list, without proof, the implications of the OS.Ni=2 assignment on the physical properties.

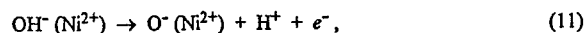
### A. Charging reactions

The overall reaction in the charging of the nickel oxide electrode (NOE) is, in the

simplest form,

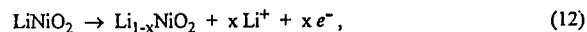


where the  $\text{H}^+$  ion and electron,  $e^-$ , move outside of the NOE material. Relying on the ionic picture of the  $\text{OS.Ni=IOS.Ni}$ , this reaction has been viewed as oxidation of  $\text{Ni}^{2+}$  into the higher oxidation states,  $\text{Ni}^{3+}$  and/or  $\text{Ni}^{4+}$ . According to the new assignment of  $\text{OS.Ni=2}$ , it should be viewed as oxidation of  $\text{O}^{2-}$ , namely,

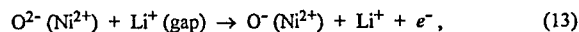


where  $(\text{Ni}^{2+})$  reminds us that the  $\text{OH}^-$  and  $\text{O}^-$  anions are attached to the  $\text{Ni}^{2+}$  ion, which remains unchanged.

Similarly, the charging reaction of another battery material  $\text{LiNiO}_2$  is given by



where the  $\text{Li}^+$  ion and electron,  $e^-$ , leave the  $\text{LiNiO}_2$  material. Again relying on  $\text{OS.Ni=IOS.Ni}$ , this reaction has been viewed as oxidation of the  $\text{Ni}^{3+}$  into  $\text{Ni}^{4+}$  [3]. According to the  $\text{OS.Ni=2}$  assignment, it should be viewed as oxidation of the  $\text{O}^{2-}$ ,



where the  $\text{Li}^+$  (gap) means that the  $\text{Li}^+$  ion is in the van der Waals gap of the  $\text{NiO}_2$  slabs.

### B. Color change

Upon charging NOE  $[\text{Ni(OH)}_2]$ , its color (pale green) turns to black, the apparent color of  $\beta\text{-NiO(OH)}$  and  $\gamma\text{-NiOOH}$  [17, 18]. Assuming  $\text{OS.Ni=IOS.Ni}$ , this coloration has been attributed to the  $2p(\text{O}^{2-}) \rightarrow 3d(\text{Ni}^{3+})$ , oxygen-to-metal, charge transfer in the charged NOE [18]. On the other hand, the  $\text{OS.Ni=2}$  assignment suggests another

possibility of  $3d(Ni^{2+}) \rightarrow 2p(O^-)$ , metal-to-oxygen, charge transfer for the strong optical absorption in the charged NOE. We favor the latter, the metal-to-oxygen charge transfer, based on the argument given in the APPENDIX A.

### C. Electron conduction

On the premise of  $OS.Ni=IOS.Ni$ , electron conduction in the NOE has to take place in the Ni layer for both the charged and discharged NOE, because every oxygen ion has a closed electronic structure of  $O^{2-}(2p^6)$ . On the other hand, the  $OS.Ni=2$  assignment suggests electronic conduction in the oxygen layer for the charged NOE though the holes of the  $O^-(2p^5)$  ions. Electron conduction in the oxygen layer should be more efficient than that in the nickel layer, because the shortest O-O and Ni-Ni distances are equal in the NOE material but the size of the oxygen 2p orbital is much larger than that of the nickel 3d orbital. When enough  $O^-$  ions are generated, the oxygen layer could become a metallic conductor.

It is known that upon charging the NOE, the electrical conductivity increase three orders of magnitudes [17]. Also, upon overcharging, sometimes, a layer with metallic luster has been observed [19, 20]. These may be due to the electronic conduction in the oxygen layer.

### D. Crystal structure

It is known that the  $Li_{0.5}NiO_2$  compound has at least two polymorphs, the *layered*  $Li_{0.5}NiO_2$  and cubic *spinel*  $Li[Ni_2]O_4$  structures [13]. In both structures, Ni is octahedrally coordinated by oxygen atoms, but the spinel  $Li[Ni_2]O_4$  has a 3D-networked structure whereas the layered  $Li_{0.5}NiO_2$  has a 2D-layered structure. The layered  $Li_{0.5}NiO_2$  is metastable and can be converted into the more stable  $Li[Ni_2]O_4$  by heating around 250°C [13]. In this conversion process, one quarter of the Ni from the  $NiO_2$  slabs



of the layered  $\text{Li}_{0.5}\text{NiO}_2$  move into the van der Waals gaps so as to maximize the electrostatic Madelung energy, resulting in a 3D-networked structure of  $\text{NiO}_2$ . By analogy, we speculate that the layered  $\text{NiO}_x(\text{OH})_{2-x}$  is also metastable and can be converted by heating at a high temperature into a more stable 3D-networked structure.

We believe that  $\text{NiO}_2$  also has two or more polymorphs, the layered  $\text{NiO}_2$  and the commercial  $\text{NiO}_2$  material which was supplied by Aldrich Chemical Co. (Milwaukee, WI). The layered  $\text{NiO}_2$  may be metastable and can be converted into the more stable commercial  $\text{NiO}_2$  material by heating. We suspect that the commercial  $\text{NiO}_2$  material has an amorphous 3D-networked structure, in which the Ni atoms are coordinated by oxygen anions in a tetrahedral geometry as well as octahedral. Evidence for the polymorphism in the  $\text{NiO}_2$  compound is given in APPENDIX B.

We speculate that a close relationship exists between the crystal structure (2D-layered and 3D-networked) and the electronic structure (covalent and ionic). The more stable 3D-networked polymorph has more ionic bonding, or  $\text{OS.Ni}=\text{IOS.Ni}$ , whereas the layered polymorph has more covalent bonding, or  $\text{OS.Ni}=2$ .

#### ACKNOWLEDGMENTS

We gratefully acknowledge the support of the Office of Naval research.

### APPENDIX A: Optical absorption of NOE

The absorption spectra on thin ( $< 200\text{\AA}$ ) film  $\text{Ni}(\text{OH})_2$  electrodes have been measured with *in situ* reflection [21] and transmission [18] spectroscopies. The results from the two techniques agree with each other and reveal the following characteristics:

- (i) There is virtually no absorption for the fully reduced NOE (i.e.,  $\text{Ni}(\text{OH})_2$ ) in the 300-900nm region. In contrast, the spectra of the fully charged NOE (i.e.,  $\gamma\text{-NiOOH}$ ) in this region shows a strong absorption which cannot be attributable to "forbidden" transitions such as *d-d* transitions.
- (ii) The 2-5eV absorption band consists of two features, a broad and strong band peaked around 3.0eV and a sharp but weak band peaked around 4.1eV.
- (iii) The spectra at intermediate states of charge show that the absorbency of the 2-5eV band is proportional to the charging with no new absorption bands appearing.

Below we examine the OS.Ni=2 and OS.Ni=3.5 alternate assignments for  $\gamma\text{-NiOOH}$  based on these observed characteristics (i)-(iii).

Based on the OS.Ni=2 premise, we can attribute the observed optical bands to metal-to-oxygen charge transfer,  $3d(\text{Ni}^{2+}) \rightarrow 2p(\text{O}^-)$ , more precisely,  $e_g(\text{Ni}^{2+}) \rightarrow 2p(\text{O}^-)$  and  $t_{2g}(\text{Ni}^{2+}) \rightarrow 2p(\text{O}^-)$  transitions from the ground state  $[\text{Ni}^{2+}(t_{2g}^6 e_g^2) \text{O}^{2-}(2p^5) \dots]$  of a charged NOE. The crystal field splitting of the *d* orbitals in an octahedral field  $\Delta_o$  (i.e.,  $t_{2g}$  and  $e_g$  orbital energy difference) for the first transition metals are known to be in the range of 0.9-1.6eV for divalent metals and 1.7-3.1eV for trivalent metals [22].  $\Delta_o$  for NiO solid is usually assumed to be around 1eV [23]. Band peaks due to the  $e_g(\text{Ni}^{2+}) \rightarrow 2p(\text{O}^-)$  and  $t_{2g}(\text{Ni}^{2+}) \rightarrow 2p(\text{O}^-)$  transitions, therefore, will be separated by about 1eV. Furthermore, we expect that the  $e_g \rightarrow 2p$  band is broader and stronger than the  $t_{2g} \rightarrow 2p$  band. In short, the  $e_g \rightarrow 2p$  and  $t_{2g} \rightarrow 2p$  bands will have the same characteristics as the 3.0 eV and 4.1 eV

bands described in (ii).

The characteristics of (i) and (iii) can also be accounted for quite naturally by the  $3d(\text{Ni}^{2+}) \rightarrow 2p(\text{O}^-)$  assignment. The charge-transfer transitions appear only after 2p holes are created in the  $\text{O}^{2-}$  ions producing  $\text{O}^-$  ions. This immediately explains (i) why the optical absorption band appears only after the NOE is charged. The charging of the NOE in the OS.Ni=2 assignment increases the number of  $\text{O}^-$  ions but not the OS.Ni value. Consequently the absorbency, i.e., the amplitude of the  $3d(\text{Ni}^{2+}) \rightarrow 2p(\text{O}^-)$  bands, increases proportionally to the charging, but the shape of the absorption bands is independent of the charging, since the same  $3d(\text{Ni}^{2+}) \rightarrow 2p(\text{O}^-)$  transitions are involved throughout the charging as observed (iii). To sum up, the observations (i)-(iii) are consistent with the OS.Ni=2 assignment for  $\gamma$ -NiOOH.

On the other hand, the explanations of (i)-(iii) based on the OS.Ni=3.5 premise for  $\gamma$ -NiOOH is problematic. The 2-5 eV band has been previously [18, 21] attributed to the oxygen-to-metal charge transfer,  $2p(\text{O}^{2-}) \rightarrow 3d(\text{Ni}^{3+})$ , on the analogy of the absorption spectrum of  $\text{Ni}^{3+}$  ions in corundum ( $\text{Al}_2\text{O}_3$ ), which exhibits two relatively narrow (FWHM  $\approx 0.7$  eV) and almost equal amplitude bands around 3.0 and 4.5 eV [24]. The OS.Ni=3.5 premise, however, implies the presence of  $\text{Ni}^{4+}$  ions along with  $\text{Ni}^{3+}$  ions. The  $2p(\text{O}^{2-}) \rightarrow 3d(\text{Ni}^{4+})$  transition should produce another band at lower energy but such an additional band has not been observed down to 1.5 eV. This absence of the  $2p(\text{O}^{2-}) \rightarrow 3d(\text{Ni}^{4+})$  absorption band has to be explained. Another difficulty is (iii), which implies the presence of only one colored (homogeneous) species with OS.Ni=3.5. Recent studies [3, 25] on the similar system  $\text{Li}_x\text{NiO}_2$  ( $x=0-1$ ), however, indicates that  $\text{Li}_x\text{NiO}_2$  goes through at least three phases on the oxidation-reduction process. In sum, the OS.Ni=3.5 assignment for  $\gamma$ -NiOOH may not be inconsistent with (i)-(iii), but unusual explanations are required to account for them.

## APPENDIX B: Polymorphism of $\text{NiO}_2$ compound

Mansour's group has studied commercial  $\text{NiO}_2$  material (supplied by Aldrich Chemical Co., Milwaukee, WI) by X-ray diffraction (XRD) and X-ray absorption [5, 26]. The XRD spectrum shows broad bands indicative of highly disordered or amorphous materials. [Similar broad XRD bands have been reported by Melendres's group [27] for  $\text{NiO}_2$  supplied by Alfa-Ventron (Danvers, MA) and also for  $\text{NiO}_2$  samples prepared chemically following either the Bro and Cogley [28] or Nakagawa [29] procedure.] In contrast, the XRD spectrum for layered  $\text{Li}_{0.06}\text{NiO}_2$  shows sharp lines indicative of crystalline materials [3].

EXAFS analyses for the commercial  $\text{NiO}_2$  [5] yielded two Ni-O bond lengths (1.91 and 2.06 Å) with a weighted average of 1.99 Å, which is much longer than that (1.852 Å) of the layered  $\text{NiO}_2$ . Moreover, the latter has only one Ni-O bond length. The pre-edge peak of the layered  $\text{NiO}_2$  is expected to be sharp and shifted about 2 eV (judging from its Ni-O bond length) to higher energy relative to that of  $\text{NiO}$ . The pre-edge peak observed for the commercial  $\text{NiO}_2$  material is, however, broad and shifted only by  $\approx 0.7$  eV. The K-edge shift of the commercial  $\text{NiO}_2$  material is also small ( $\approx 1.3$  eV) in comparison with that (3.0 eV) of the layered  $\text{NiO}_2$  compound.

All these differences between the layered  $\text{NiO}_2$  and the commercial  $\text{NiO}_2$  material imply that they are indeed different polymorphs.

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**Table I** Summary of supporting evidence for the OS.Ni=2 and OS.Ni=IOS.Ni assignments for each compound, where OS.Ni stands for "oxidation state of nickel" and the value for the IOS.Ni (ionic OS.Ni) is given in the table.

Compound	IOS.Ni	Supporting evidence for	
		OS.Ni = 2	OS.Ni = IOS.Ni
LiNiO <sub>2</sub>	3	XPS (main peak) XPS (satellite) Ni-O (JTD) Ni-O (covalent) Oxygen K-edge XAS [15]	Magnetic moment [13, 16] Ni-O (ionic radii)
β-NiO(OH)	3	XAS (K-edge) Ni-O (JTD) Ni-O (constant)	Magnetic moment [2] Ni-O (ionic radii)
γ-"NiOOH"	3.5	XPS (main) XPS (satellite) XPS (line width) XAS (white line) XAS (k-edge) Ni-O (constant)	Magnetic moment [2] Ni-O (ionic radii)
KNiO <sub>2</sub> (IO <sub>4</sub> )	4	XPS (main) XPS (satellite) XAS (pre-edge peak) Ni-O (covalent)	Ni-O (ionic radii)
BaNiO <sub>3</sub>	4	XAS (K-edge) Ni-O (covalent)	Ni-O (ionic radii)

Ni-O (JTD) = absence of Jahn-Teller distortion.

Ni-O (constant) = constant Ni-OH and Ni-O bond lengths.

Ni-O (ionic radii) = sum of ionic radii.

Ni-O (covalent) = covalent shortening.

XPS = x-ray photoemission spectroscopy

XAS = x-ray absorption spectroscopy.

### FIGURE CAPTIONS

**FIG. 1.** Ni-O distances of the Ni-OH (open circle) and Ni-O (closed circle) bonds observed for  $\text{NiO}_x(\text{OH})_{2-x}$  [ $x=0, 1$ , and  $1.5$ ] as a function of the IOS.Ni along with the Ni-O bond lengths for the IOS.Ni $\approx$ 4 compounds,  $\text{Li}_{0.06}\text{NiO}_2$ ,  $\text{KNiO}_2(\text{IO}_4)$ , and  $\text{BaNiO}_3$ . The dashed and dotted lines are respectively the variations of the Ni-OH and Ni-O bond lengths predicted on the OS.Ni=IOS.Ni premise. The solid lines are those predicted on the OS.Ni=2 premise.

**FIG. 2.** Mean Ni-O distance for the compounds in Fig. 1 plotted as a function of the IOS.Ni. A large deviation from the linear relationship for  $\gamma$ -NiOOH is due to experimental difficulty (see the text). The dashed line is an averaged sum of the ionic radii assuming the OS.Ni=IOS.Ni. The solid line is the variation predicted assuming the OS.Ni=2.

**FIG. 3.** Ni-O bond length for the Ni-LiNiO<sub>2</sub>-NiO<sub>2</sub> series plotted as a function of the IOS.Ni. The dashed line is obtained as a sum of the ionic radii assuming OS.Ni=IOS.Ni. The solid line is the variation of the Ni-O bond length predicted assuming OS.Ni=2. It is shown in the text that this variation is due to a covalent shortening.

**FIG. 4.** The relationship between the symmetric stretching potential curves,  $V^{(0)}(R)$  and  $V^{(1)}(R)$ , for the ground  $\text{Ni}^{2+}\text{O}_6^{2-}$  state and the ionized  $\text{Ni}^{2+}\text{O}_6^-$  state. The difference,  $V^{(1)}(R)-V^{(0)}(R)$ , gives the ionization energy,  $\text{IE}(R)$ , which varies slowly with  $R$  in comparison with the  $V^{(0)}(R)$  and  $V^{(1)}(R)$  functions.

**FIG. 5.** The M-O distances of the M-OH (thin solid line) and M-O (thick solid line) bonds in  $\text{MO}(\text{OH})$  for  $\text{M}=\text{Al}$ ,  $\text{Ni}$ , and  $\text{Mn}$ . The M-OH and M-O bond lengths for  $\text{MnO}(\text{OH})$  are splitted due to the Jahn-Teller distortion.



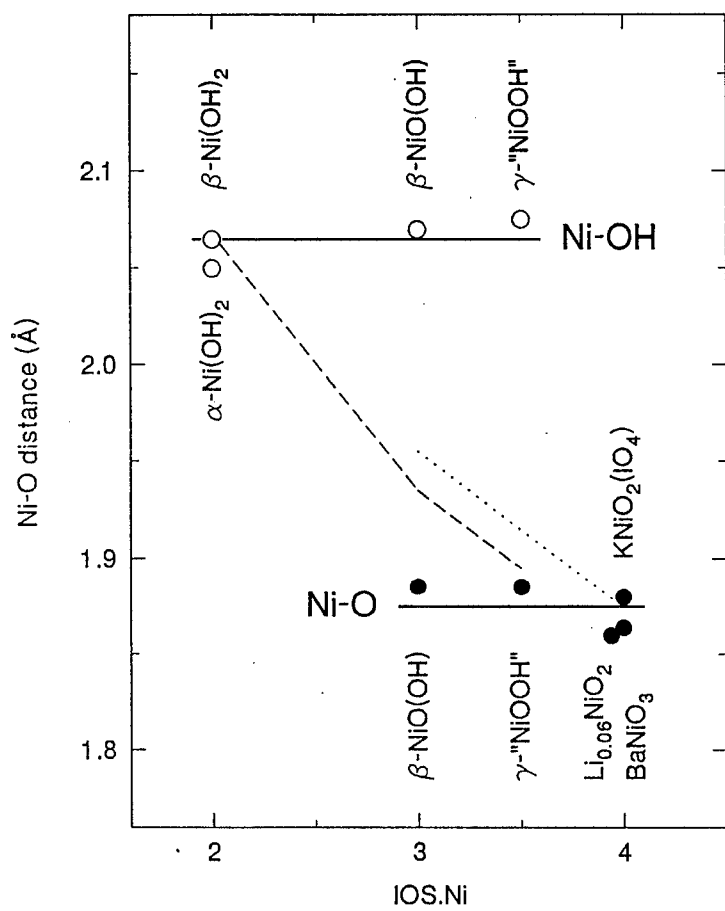


Fig. 1

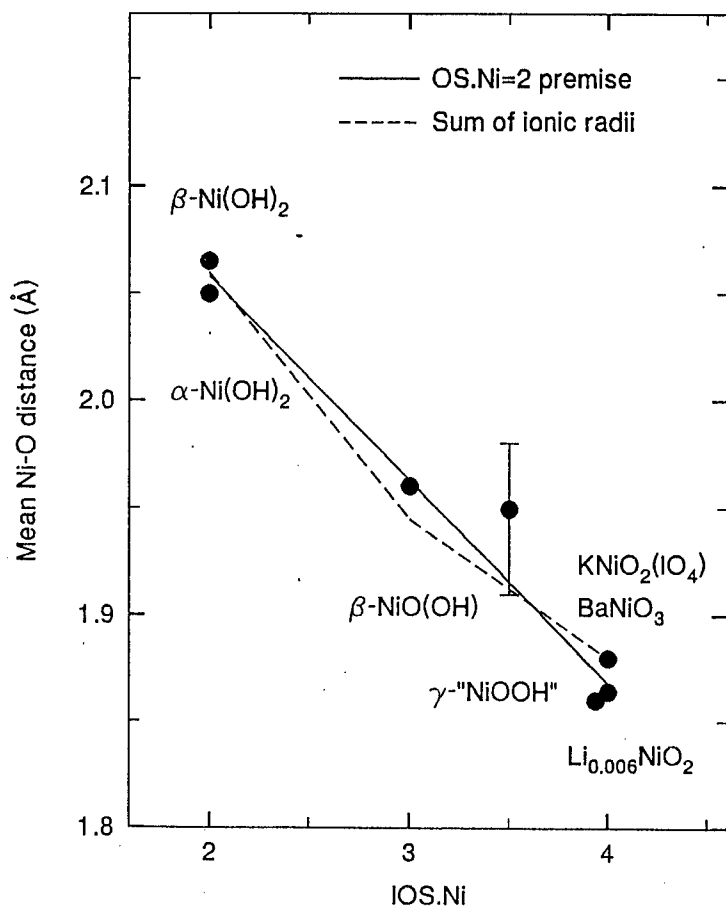


Fig. 2

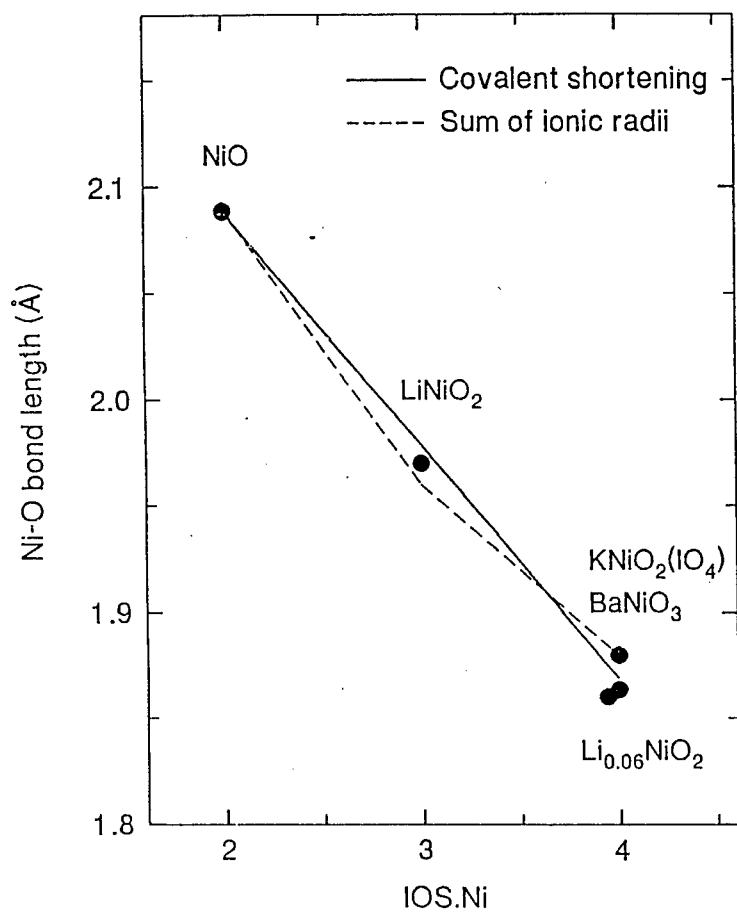


Fig. 3

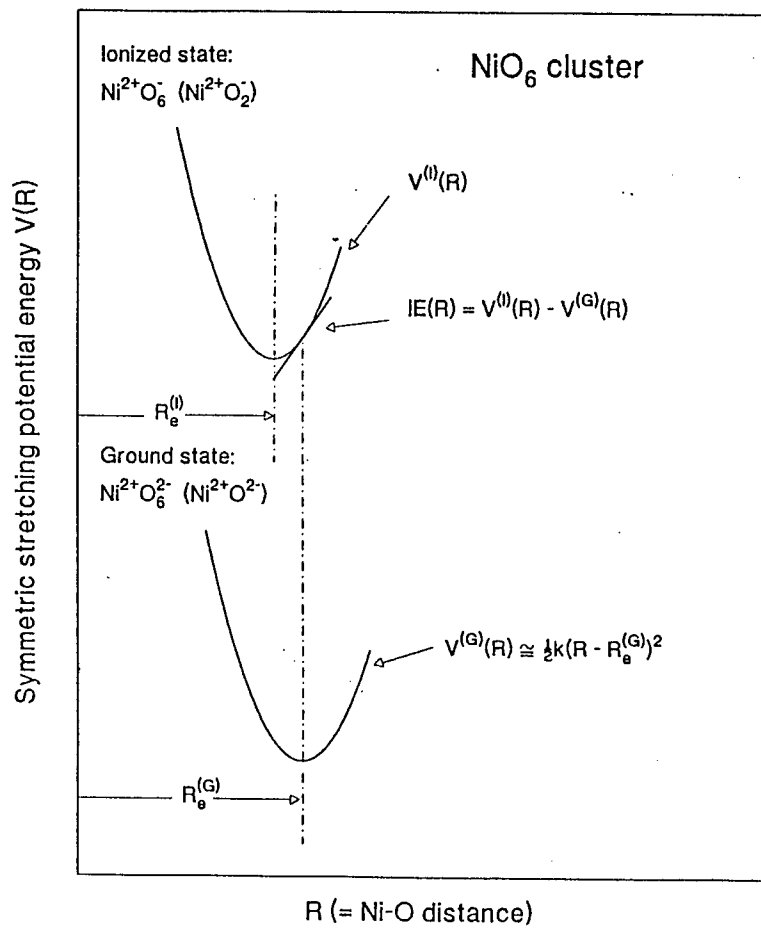


Fig. 4

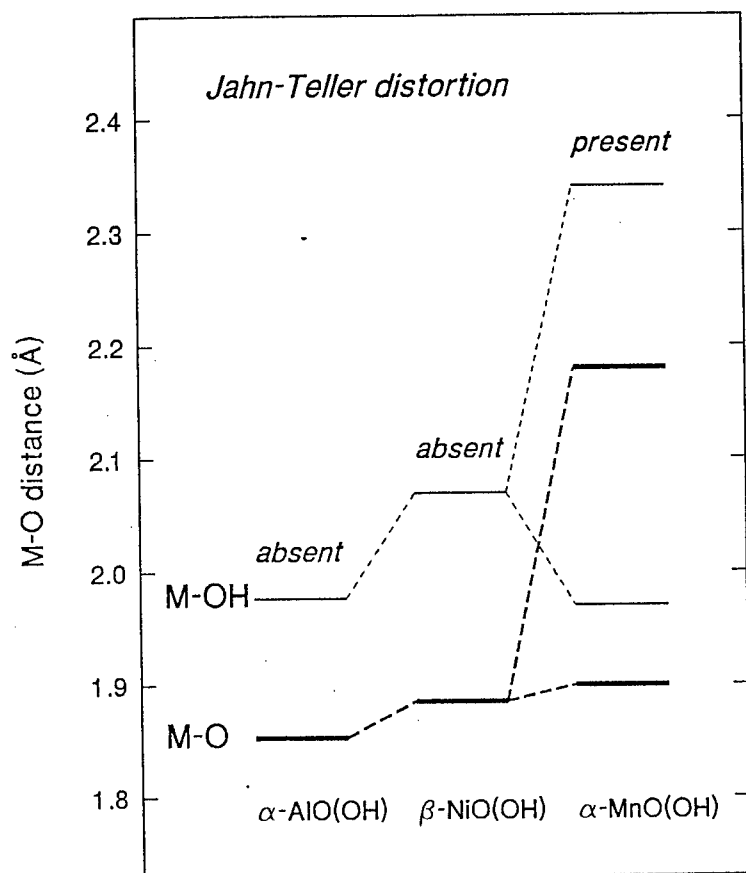


Fig. 5

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